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# PATENT SPECIFICATION

760,002

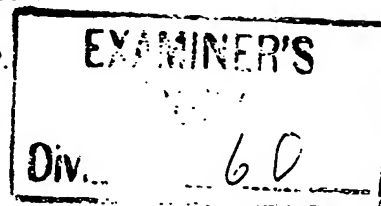
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P2C14A, P2D(1A : 2A), P2K(7 : 8), P2T2A, P7C13(A : B : C), P7C14A, P7D(2A1 : 2A2B : 3),  
P7K(2 : 7), P7T2(A : D : X) ; and 70, Q5B.

## COMPLETE SPECIFICATION.

### Reinforced Rubber Compositions and Reinforcing Materials therefor.

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 1 Albany Street, London, N.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to reinforced rubber compositions and to the production thereof, and to novel reinforcing agents.

It is an object of the present invention to provide novel rubber compositions. It is also an object to provide novel reinforcing agents for rubber.

According to the present invention a resin consists of an anionic thermoplastic or resol type resin residue having a cationic long-chain radical containing at least ten atoms in the chain attached thereto by a salt-like linkage. By the term "resol type resin" in this Specification we mean a phenol-aldehyde resin which is in the form of a liquid, hardenable by heat to a final infusible and insoluble condition.

The invention also includes novel rubber compositions comprising natural or synthetic rubber reinforced with such resins.

According to a further feature of the invention resins suitable for use as reinforcing agents for rubber are made by effecting ion exchange between anionic thermoplastic or resol type resin possessing hydrophilic ionisable groups and an organic compound containing an ionisable group comprising a long chain radical containing at least ten atoms in the chain, the polarity of the ionised resin being opposite to that of the ionisable group of the said organic compound.

The resin subjected to ion-exchange may be an anionic type resin, of the novolak or resol type, the phenolic hydroxy groups of

which are hydrophilic and ionisable by virtue of the acidic character of the hydrogen thereof, the latter being thus replaceable by other cations. Anionic resins containing sulphonic groups which are more strongly acidic than the phenolic groups, may also be used, particularly novolak or resol type resins containing sulphonic groups and sulphonated polystyrene resins. The sulphonated phenolic resins may be made by known methods, as for example by condensing a mixture of phenol and a phenol sulphonic acid with formaldehyde or hexamethylene tetramine, condensation being carried out so that a novolak or resol product is obtained.

Sulphonated polystyrene resins may be made by subjecting polystyrene to sulphonation while dispersed in a liquid sulphonating medium. For example styrene may be polymerised in aqueous emulsion and the finely divided product recovered from emulsion, e.g. by drying at a temperature below that at which the particles of resin commence to sinter. The dried product is dispersed in 98% sulphuric acid or oleum as the sulphonating medium and sulphonation then effected by heating at 70° C. in the presence of silver sulphate as catalyst. After sulphonation the sulphated product may be allowed to settle, separated by decantation, washed on a centrifuge and then dried. Preferably the sulphonation is not carried so far that the sulphonated product is water-soluble. To facilitate the production of water-insoluble sulphonated product it is preferred to use a polystyrene which is cross-linked to a small degree; such a polystyrene may be made by copolymerising preferably in an aqueous medium, styrene and a small proportion, e.g. 0.1% to 5% preferably about 2%, of a monomeric compound containing two vinyl groups

[Price 3s. 0d.]

in the molecule, e.g. divinyl benzene. The copolymers should be in a thermoplastic state.

Starting from anionic resins, for example  
5 sulphonated phenolic resins or sulphonated polystyrene resins, resins suitable for incorporation in rubber may be made by base exchange with cationic compounds containing long chain radicals with an aliphatic  
10 carbon chain, frequently called cationic soaps. Examples of these compounds are quaternary ammonium compounds.

The organic compound having the cationic long chain radical is preferably a quaternary  
15 compound having a long chain attached to the quaternary atom, e.g. a nitrogen atom. The long chain should contain at least 10 atoms excluding side chains. The atoms may be all carbon atoms or the carbon chain  
20 may be interrupted by oxygen atoms forming ether linkages between shorter carbon chains. The long chain is preferably aliphatic but may comprise a benzene ring containing aliphatic substituents, in which the benzene  
25 ring is counted as 4 carbon atoms. As well as quaternary ammonium compounds the corresponding derivatives of other tetravalent or pentavalent atoms may be employed; for example the corresponding phosphonium,  
30 oxonium or stannonium compounds.

Particularly suitable are quaternary ammonium compounds of the type  $R_1R_2R_3R_4N-X$  where X is halogen,  $R_1$  is  
35 an alkyl radical containing from 10 to 20 carbon atoms or a radical containing at least 10 atoms having a terminal alkyl-substituted aryl group and containing at least two alkylene groups linked by ether linkages,  $R_2$  is an aryl or aralkyl radical or an alkyl radical,  
40 and  $R_3$  and  $R_4$  are aryl radicals. Examples of such compounds are cetyl trimethyl ammonium bromide, dodecyl trimethyl ammonium bromide, octadecyl trimethyl ammonium bromide, cetyl benzyl dimethyl  
45 ammonium chloride, lauryl benzyl dimethyl ammonium bromide, *p-tert-octyl-phenoxy-ethoxy-ethyl* dimethyl benzyl ammonium bromide, and *p-tert-octyl-m-methyl-phenoxy-ethoxy-ethyl* dimethyl benzyl ammonium  
50 chloride.

The base exchange reaction between an anionic phenolic resin, e.g. a sulphonated novolak type phenolic resin, and the cationic  
55 soap, e.g. cetyl pyridinium chloride, may be effected by forming a dispersion of the resin in water and adding the cationic soap to the dispersion. The resultant dispersion may then be mixed directly with a rubber latex and the resin and the rubber coprecipitated  
60 as by additions of an acid. The dispersion of the resin may also be mixed with rubber latex before effecting base exchange, dispersing agents being used for dispersing the resin which will give a dispersion compatible with  
65 the latex, and the base exchange is then

effected in the presence of the latex and the rubber and cation-exchanged resin coprecipitated. However, it is preferred to effect the  
70 base exchange with the resin in dispersed form as described above, and to isolate the cation-exchanged resin and incorporate it with rubber on a heated mill or in an internal mixer. If the rubber and the resin are coprecipitated and the coprecipitate isolated,  
75 it is preferred to work the latter on a hot mill to assist in dispersing the resin in the rubber.

It is preferred that the cation-exchanged resin which is incorporated in the rubber  
80 should be a novolak or resol type resin, since better dispersion of the resin in the rubber results and thus better reinforcement. If the cation-exchanged resin is a novolak type resin hardening of the resin may be brought about by reacting it during or, preferably, subsequent to its incorporation in  
85 the rubber with a hardening agent, e.g. hexamethylene tetramine. A resol-type resin may also be incorporated in rubber, hardening the occurring concurrently with incorporation.  
90

In addition to incorporating the cation-exchanged resin in the rubber other compounding ingredients may also be incorporated,  
95 including sulphur and a vulcanisation accelerator, the composition being then moulded and vulcanised. There may also be incorporated in the vulcanisable composition other reinforcing materials, e.g. carbon black, finely divided silica, lignin,  
100 humic acid and polyvinyl compounds, and when lignin or humic acid is incorporated it may be reacted after dispersion of the resin in the rubber or before incorporation in the rubber with a methylene donor, e.g. hexa-  
105 methylene tetramine. Methods of incorporating materials of the above type are the subject of Patent Specifications Nos. 691,608, 702,670, 709,991, 713,531, 723,897 and 723,898 and Patent Application No. 110  
13255/51.

The synthetic rubber may be a conjugated diene polymer or a copolymer of a conjugated diene with a compound copolymerisable therewith, e.g. polybutadiene, poly-  
115 chloroprene or a copolymer of butadiene with isobutylene, acrylonitrile or styrene. Vulcanisable reclaims of these rubbers or of natural rubber may be used and also oil-modified synthetic rubbers, particularly  
120 butadiene/styrene copolymers, in which extender oils have been dispersed. The rubber may also be an oil-modified natural rubber of the type described in co-pending Application No. 407/52.  
125

The invention is illustrated by the following Examples in which all parts are by weight:—

#### EXAMPLE 1.

Six molecular proportions of phenol, one 130

- of phenolsulphonic acid and five of formaldehyde were dissolved in an equal weight of water and the pH of the solution raised to 1.8 by the addition of sodium hydroxide.
- 5 The solution was then heated under reflux for  $1\frac{1}{2}$  hours in a suitable reaction vessel. Water was then removed by distillation under reduced pressure. Throughout the preparation of the resin, the temperature of the heating bath was maintained at  $110^{\circ}$ — $115^{\circ}$  C.
- 10 The distillation was stopped when a sample of the resinous product became brittle on cooling to  $25^{\circ}$  C. The resinous product was then removed, ground to a fine powder,
- 15 washed free of water-soluble matter and dried. 100 parts of the finely powdered resin were suspended in water and to the suspension was added an aqueous solution of 10 parts of cetyl trimethyl ammonium bromide. After 10 minutes the precipitated matter was removed by filtration, washed and dried.
- 20 33 parts of the cation-exchanged resin prepared as above (approximately equivalent to 30 parts of the original resin) were then incorporated into 100 parts of natural rubber on a roll mill heated to a temperature equal to that of saturated steam at a pressure of 10 lb./sq. in. The resulting batch was then
- removed from the mill and allowed to cool. 30  
A sufficient quantity was then replaced on a cool mill and vulcanising ingredients added to yield a compounded rubber of the following composition:—
- |                        |     |     |           |    |
|------------------------|-----|-----|-----------|----|
| Rubber                 | ... | ... | 100 parts | 35 |
| Cation-exchanged resin | ... | ... | 33 parts  |    |
| Stearic acid           | ... | ... | 2 parts   |    |
| Zinc oxide             | ... | ... | 5 parts   |    |
| Sulphur                | ... | ... | 3 parts   |    |
| Mercaptobenzthiazole   | ... | ... | 1 part    | 40 |
- Suitable test pieces were then prepared by vulcanising the resulting compounded rubber in moulds at a temperature equal to that of saturated steam at a pressure of 60 lb./sq. in., the heating-up period being 15 minutes and the heating then being continued for 35 minutes. 45
- As a control a rubber compound similar to the above was prepared except that in place of the 33 parts of cation-exchanged resin, 30 parts of the unmodified resin were used, and suitable test pieces were formed in the same way. The curing period in this case was 15 minutes heating-up and 60 minutes at 60 lb./sq. in. 50
- The following test figures were obtained: 55

	<i>Compound containing unmodified resin</i>	<i>Compound containing cation-exchanged resin</i>
Stress at 300% elongation lb./sq. in. ...	265	375
60 Stress at 500% elongation lb./sq. in. ...	800	1155
Tensile Strength lb./sq. in. ...	1795	2030
Elongation at break % ...	710	675
Tear Strength lb./sq. in. ...	120	150
British Standard Hardness degrees ...	37	44
65 Resilience % ...	81	89

#### EXAMPLE II.

- Using a further portion of the unmodified resin prepared as in Example I, a further quantity of cation-exchanged resin was prepared according to the procedure there described but using cetyl pyridinium chloride in place of cetyl trimethyl ammonium bromide.
- 70 The resulting modified resin was then used in the manner described in Example I to prepare a rubber compound of the same general composition as that described therein.
- 75 Suitable test pieces were then prepared from the rubber compound by heating in moulds in an atmosphere of saturated steam under conditions such that the pressure of steam was raised from atmospheric to a gauge pressure of 40 lb./sq. in. in 15 minutes and was maintained at 40 lb./sq. in. for a further period of 60 minutes. 80
- As a control, test pieces were prepared in the same manner using a rubber compound containing 30 parts of the unmodified resin in place of the cation-exchanged resin. 85
- The following test figures were obtained:

	<i>Compound containing unmodified resin</i>	<i>Compound containing cation-exchanged resin</i>
Stress at 300% elongation lb./sq. in. ...	300	520
Stress at 500% elongation lb./sq. in. ...	875	1455
Tensile Strength lb./sq. in. ...	1835	1980
95 Elongation at break % ...	701	610
Tear Strength lb./sq. in. ...	100	110
British Standard Hardness degrees ...	43	50
Resilience % ...	85	90

What we claim is:—

- 100 1. A resin which consists of an anionic thermoplastic or resol type resin residue having a cationic long-chain radical contain-

ing at least ten atoms in the chain attached thereto by a salt-like linkage.

2. A resin according to Claim 1 wherein the said residue is that of a phenolic resin in which the phenolic hydroxy groups are hydrophilic and ionisable.

3. A resin according to Claim 1 or 2 wherein the said residue is that of a resin of the novolak type.

4. A resin according to Claim 1 wherein the said residue is that of a sulphonated polystyrene resin.

5. A method of producing a resin according to any of Claims 1 to 4 which comprises effecting ion-exchange between an anionic thermoplastic or resol type resin possessing hydrophilic ionisable groups and an organic compound containing an ionisable group comprising a long-chain radical containing at least ten atoms in the chain, the polarity of the resin when ionised being opposite to that of the ionisable group of the said organic compound.

6. A method according to Claim 5 wherein the said anionic thermoplastic or resol resin is sulphonated.

7. A method according to Claim 5 or 6 wherein the said anionic resin is a novolak.

8. A method according to Claim 5 or 6 wherein the said anionic resin is a sulphonated polystyrene resin.

9. A method according to Claim 5, 6, 7 or 8 wherein the said organic compound is a quaternary ammonium compound possessing a long chain radical containing at least ten atoms in the chain attached to the nitrogen atom thereof.

10. A method according to Claim 9 wherein the long chain is aliphatic.

11. A method according to Claim 9 wherein the said long chain is composed of carbon atoms or of carbon chains linked by oxygen atoms.

12. A method of preparing a reinforced rubber composition which comprises incorporating in natural or synthetic rubber a resin prepared in accordance with any of Claims 5 to 11.

13. A method according to Claim 12 which comprises producing a resin in accordance with the method of any of Claims 5 to 11 and incorporating the resin in the rubber by milling on hot rolls.

14. A reinforced rubber composition comprising natural or synthetic rubber having incorporated therein a finely divided resin according to any of Claims 1 to 4.

15. A reinforced natural or synthetic rubber composition when prepared according to Claim 12 or 13.

16. A resin in which the macromolecular structure has long-chain radicals containing at least ten atoms in the chain attached thereto by a salt like linkage when prepared in accordance with any of Claims 5 to 11.

17. A method of preparing a reinforced natural or synthetic rubber composition substantially as described in the foregoing Examples.

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Agent for the Applicants.

#### PROVISIONAL SPECIFICATION.

#### Reinforced Rubber Compositions and Reinforcing Materials therefor.

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 1 Albany Street, London, N.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to reinforced rubber compositions and to the production thereof, and to novel reinforcing agents.

It is an object of the present invention to provide novel rubber compositions. It is also an object to provide novel reinforcing agents for rubber.

According to the present invention novel rubber compositions comprise a natural or synthetic rubber reinforced with a finely divided resin having long chain radicals comprising an aliphatic carbon chain. Preferably the rubber is reinforced with a finely divided synthetic resin in which the macromolecular skeleton thereof has long side chain radicals comprising an aliphatic carbon

chain attached to the skeleton by a salt-like linkage.

According to a further feature of the invention novel reinforcing agents for rubber are made by effecting ion exchange between a thermoplastic or heat-hardenable resin having hydrophilic ionisable groups and an organic compound having an ionisable group comprising a long chain radical containing an aliphatic carbon chain, the polarity of the ionised resin being opposite to that of the ionisable group with a long chain radical.

The resin subjected to base-exchange may be an anionic type resin, for example, a novolak type or resol type phenolic resin, the phenolic hydroxy groups of which are hydrophilic and ionisable by virtue of the acidic character of the hydrogen thereof, the latter being thus replaceable by other cations. Anionic resins containing sulphonic groups, which are more strongly acidic than the phenolic groups, may also be used, particu-

larly novolak type or resol type phenolic resins containing sulphonic groups and sulphonated polystyrene resins. The sulphonated phenolic resins may be made by known methods, as for example by condensing a mixture of phenol and a phenol sulphonic acid with formaldehyde or hexamethylene tetramine, condensation being carried out so that a novolak or resol product is obtained.

Sulphonated polystyrene resins may be made by subjecting polystyrene to sulphonation while dispersed in a liquid sulphonating medium. For example styrene may be polymerised in aqueous emulsion and the finely divided product recovered from emulsion, e.g. by drying. The dried product dispersed in 98% sulphuric acid or oleum as the sulphonating medium, and sulphonation then effected by heating at 100° C. in the presence of silver sulphate as catalyst. After sulphonation the sulphonated product may be allowed to settle, separated by decantation and washed on a centrifuge and then dried. Preferably the sulphonation is not carried so far that the sulphonated product is water-soluble. To facilitate the production of water-insoluble sulphonated product it is preferred to use a polystyrene which is cross-linked to a small degree; such a polystyrene may be made by copolymerising, preferably in an aqueous medium, styrene and a small proportion, e.g. 0.1% to 5%, of monomeric compound containing two vinyl groups in the molecule, e.g. divinyl benzene.

Starting from anionic resins, for example sulphonated phenolic resins or sulphonated polystyrene resins, resins suitable for incorporation in the rubber may be made by base exchange with cationic compounds containing long chain radicals with an aliphatic carbon chain, frequently called cationic soaps. Examples of these compounds are quaternary ammonium compounds.

The organic compound having the cationic long chain radical is preferably a quaternary ammonium compound having a long chain attached to the nitrogen atom. The long chain may be aliphatic and should contain at least 10 atoms in the chain. These may be all carbon atoms or the carbon chain may be interrupted by oxygen atoms forming other linkages between shorter carbon chains. The long chain may comprise a benzene ring containing aliphatic substituents. As well as quaternary ammonium compounds the corresponding derivatives of other tetravalent or pentavalent atoms may be employed for example the corresponding phosphonium, oxonium or stannonium compounds.

Particularly suitable are quaternary ammonium compounds of the type  $R_1R_2R_3R_4N-X$  where X is halogen,  $R_1$  is an alkyl radical containing from 10 to 20 carbon atoms or a radical having a terminal alkyl-substituted aryl group and containing

at least two alkylene groups linked by ether linkages,  $R_2$  is an aryl or aralkyl radical or an alkyl radical, and  $R_3$  and  $R_4$  are alkyl radicals. Examples of such compounds are cetyl trimethyl ammonium bromide, dodecyl trimethyl ammonium bromide, octadecyl trimethyl ammonium bromide, cetyl benzyl dimethyl ammonium chloride, lauryl benzyl dimethyl ammonium bromide, *p-tert-octyl*-phenoxy-ethoxy-ethyl dimethyl benzyl ammonium bromide, and *p-tert-octyl*-*m*-methyl-phenoxy-ethoxy-ethyl dimethyl benzyl ammonium chloride.

The base exchange reaction between an anionic phenolic resin, e.g. a sulphonated novolak type phenolic resin, and the cationic soap, e.g. cetyl pyridinium chloride may be effected by forming a dispersion of the resin in water and adding the cationic soap to the dispersion. The resultant dispersion may then be mixed directly with a rubber latex and the resin and the rubber coprecipitated as by additions of an acid. The dispersion of the resin may also be mixed with rubber latex before effecting base exchange, dispersing agents being used for dispersing the resin which will give a dispersion compatible with the latex, and the base exchange is then effected in the presence of the latex and the rubber and cation-exchanged resin coprecipitated. It is also possible to effect the base exchange with the resin in dispersed form as described above, and to isolate the cation-exchanged resin and incorporate it with rubber on a mill or in an internal mixer. If the rubber and the resin are coprecipitated and the coprecipitate isolated, it is preferred to work the latter on a mill to assist in dispersing the resin in the rubber.

It is preferred that the resin having long chain substituents with aliphatic chains which is incorporated in the rubber should be thermoplastic or a novolak type resin, since better dispersion of the resin in the rubber results and thus better reinforcement. If the resin is a novolak type resin hardening of the resin may be brought about by reacting it during or, preferably, subsequent to its incorporation in the rubber with a hardening agent, e.g. hexamethylene tetramine. A resol type resin having long chain substituents with aliphatic chains may also be incorporated in rubber, hardening then occurring concurrently with incorporation. It is also within the scope of the invention to incorporate in rubber a finely divided thermoset resin having long chain substituents with aliphatic chains. Such resins may, for example, be made from finely divided particles of a thermoset sulphonated phenolic resin by suspending or dispersing the particles in an aqueous medium and adding a cationic soap thereto.

In addition to incorporating the resin

having long chain substituents with aliphatic chains in the rubber other compounding ingredients may also be incorporated, including sulphur and a vulcanisation accelerator, the composition being then moulded and vulcanised. There may also be incorporated in the vulcanisable composition other reinforcing materials, e.g. carbon black, finely divided silica, lignin, humic acid and polyvinyl compounds, and when lignin or humic acid is incorporated it may be reacted after dispersion of the resin in the rubber or before incorporation in the rubber with a methylene donor, e.g. hexamethylene tetramine. Methods of incorporating materials of the above type are the subject of co-pending Application No. 13255/51 and Patent Specifications Nos. 691,608, 702,670, 713,531, 723,897 and 723,898.

The synthetic rubber may be a conjugated diene polymer or a copolymer of a conjugated diene with a compound copolymerisable therewith, e.g. polybutadiene, polychloroprene or a copolymer of butadiene with isobutylene, acrylonitrile or styrene. Vulcanisable reclaims of these rubbers or of natural rubber may be used and also oil-modified synthetic rubbers, that is to say unvulcanised synthetic rubbers, particularly butadiene/styrene copolymers, in which extender oils have been dispersed. The rubber may also be an oil-modified natural rubber of the type described in co-pending Application No. 407/52.

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